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Novel Approaches towards Highly Selective Self-Powered Gas Sensors

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Abstract

The prevailing design approaches of semiconductor gas sensors struggle to overcome most of their current limitations such as poor selectivity, and high power consumption. Herein, a new sensing concept based on devices that are capable of detecting gases without the need of any external power sources required to activate interaction of gases with sensor or to generate the sensor read out signal. Based on the integration of complementary functionalities (namely; powering and sensing) in a singular nanostructure, self-sustained gas sensors will be demonstrated. Moreover, a rational methodology to design organic surface functionalization that provide high selectivity towards single gas species will also be discussed. Specifically, theoretical results, confirmed experimentally, indicate that precisely tuning of the sterical and electronic structure of sensor material/organic interfaces can lead to unprecedented selectivity values, comparable to those typical of bioselective processes. Finally, an integrated gas sensor that combine both the self-powering and selective detection strategies in one single device will also be presented.

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Keywords: self-powered; gas sensor; semiconductors; selectivity; integrated nanodevices, self assembled monolayers.

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1. Introduction

Development of ultra-low power or self-powered gas sensors with a high selectivity toward certain gases is required for their integration in smart mobile devices for environmental monitoring and hazardous gas detection [1]. Recent reports have shown promising concepts to realize self-powered gas sensors that are capable of detecting gases at zero power, which was achieved through designing heterostructure interfaces capable of harvesting solar light needed to drive the sensing signal as well as providing the activation energy needed for gas/sensor interactions [2–5]. While, sensor selectivity remains a challenging issue that need to be addressed. As a result of their nonselective sensing mechanism based on redox interaction with gas molecules, gas sensors based on pure inorganic show poor selectivity [6]. Recently bioinspired approaches have found their way into gas sensing application due to the appealing analogies between both fields [7,8]. High selectivity toward a single gas species can be achieved via the binding of the analyte to recognition surface elements, which is capable of specifically recognizing and binding with the target analyte [9]. In this respect, modifying the inorganic semiconductors surface with self-assembled monolayers (SAMs) have attract an increased interest in different fields of applications such as biosensors, biomolecular electronics, and gas sensors due to their rich and tunable functionalities which could provide a selective binding interaction between these organic receptor and target molecular species [9,10].

In this work, a highly selective NO_2 sensor is realized based on self-assembled monolayer (SAM)-modified ZnO nanowires (NW). The energetic position of the frontier orbitals of SAM–gas interface with respect to the NW Fermi level has been identified to be the key factor to ensure or impede the charge transfer between the NW and the gas molecules and thus to discriminate a certain gas species. Herein, the first attempts to combine both self-powering and selective detection approaches in a singular integrated sensor device will be presented. A selective and self-powered gas sensor, capable of detecting low NO_2 concentrations in the ppb range without the need of an external power source will be introduced. Nitrogen dioxide is implicated in a range of impacts on human health as well as air pollution and environmental problems. As a member of highly reactive gases family called nitrogen oxides (NOx), NO_2 represent wide spread dangerous global pollutant that reacts in the air to form acid rain (corrosive nitric acid), as well as toxic organic nitrates [10,11]. Here in, the above mentioned two sensing approaches and their combination in a singular unit will be presented as following.

2. Self-powering of gas sensor devices:

External power is usually applied to metal oxide gas sensors devices in order to provide two functions. Firstly, to generate the sensor read out signal which is derived by applying a constant bias currents and monitoring the resistance changes upon exposure of different gases. Secondly, to provide the activation energies necessary for the interaction of gas molecules on the oxide surface, since the gas adsorption and desorption on the surface of metal oxides are an endothermic processes. Typically, thermal heating (in the range of 200-400 ˚C) or illumination (UV-, or visible- light) are applied to provide the needed energies for surface interaction activation [12].

The self-powered sensor device presented here is based on nanostructured p-Si/n-ZnO diodes that can harvest solar light to produce an open-circuit voltage (V_{oc}), which is related to the potential at heterojunction. The reported devices were fabricated by patterning p-Si lines on the top of SiO_2 layer by reactive ion etching (RIE) followed by deposition of 20 nm of ZnO thin film selectively on the p-Si sidewalls by photolithographic methods and finally ZnO nanowires were grown by hydrothermal route. The device fabrication process is shown schematically in Figure 1 (a-d). The produced V_{oc} serve as a self-generated signal of the gas sensor [10].

In order to enhance this self-generated signal to be measurable in case of low light illumination conditions, a number of diode devices were connected in series, by evaporated Au contacts, to increase the measured V_{oc} signal, which is found to be linearly proportional to the number of diodes connected (9, 16 or 26 diodes), where the average V_{oc} experimental was about 72 ± 6 mV/diode (see figure 1e). The experimentally observed values of p-n heterojunction ($V_{oc,exp} = 72 \pm 6$ mV/diode) is much lower than the estimated theoretical V_{oc} in an ideal heterojunction ($V_{oc,theor,ideal} = 479$ mV/diode) [10]. This arises due the large current leakage caused by the defect induced recombination of carriers at the heterojunction interface due to the lattice mismatch of Si and zinc oxide and effects of device processing procedure (e.g. sputtering and etching processes). After optimizing the self-powering of the sensor devices, a surface modification with organic SAMs was used to tune the selectivity toward specific gases.

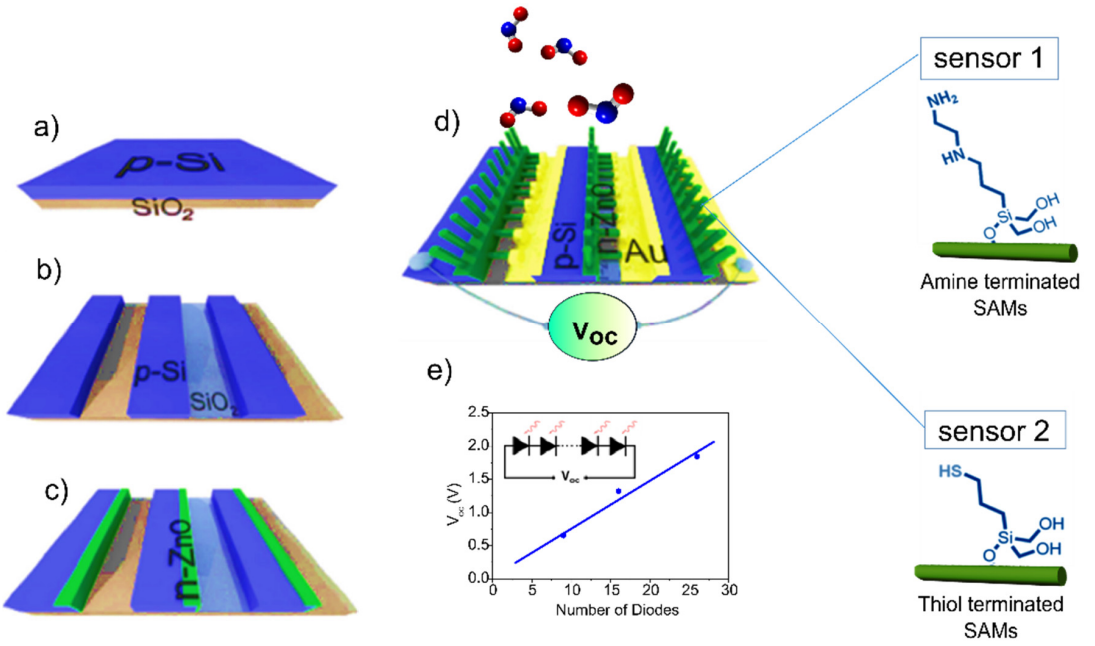

Fig. 1. Schematic representation of the device fabrication process. (a) p-Si on SiO_2; (b) p-Si lines patterning by RIE; (c) ZnO seed layer deposition; (d) n-ZnO nanowires synthesis and Au connection followed by surface functionalization by SAM with amine (Sensor 1) or thiol (Sensor 2) functional groups; (e) The relation between measured V_{oc} and the number of diodes under illuminated conditions (simulated sunlight; AM1.5).

3. Tuning the selectivity of gas sensors:

Figure 1d shows two types of methoxysilanes based SAMs that were used for surface modification of ZnO nanowires, namely amine ([3-(2-aminoethylamino)propyl]trimethoxylsilane) (Sensor 1) and thiol ((3-mercapto-propyl)trimethoxysilane) (Sensor 2). The Sensor 1 (amine functionalized sensor) device could detect different concentrations of NO_2 (250, 500, 750 ppb) in self-powered operation at low ppb values as can be seen in figure 2a,c with a linear increase of the response (ΔV_{oc}) with gas concentration.

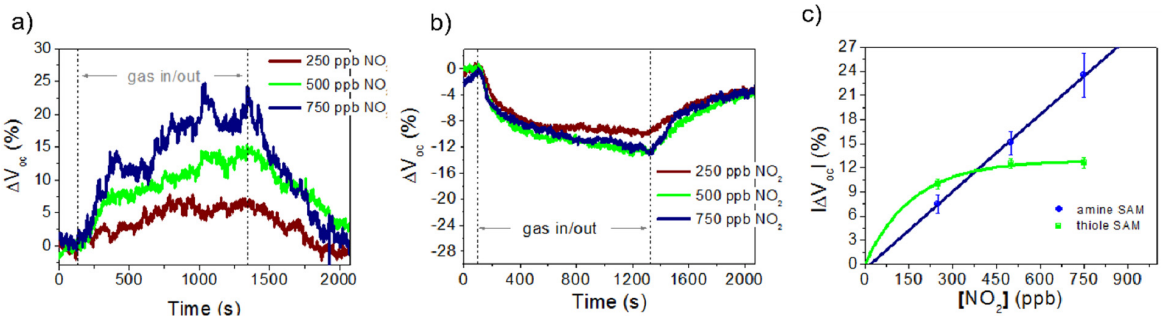

Fig. 2. Self-powered sensing response towards different concentrations of NO_2 of (a) Sensor 1; (b) Sensor 2. c) ΔV_{oc} response of amine- and thiol-functionalized sensors for different concentrations of NO_2.

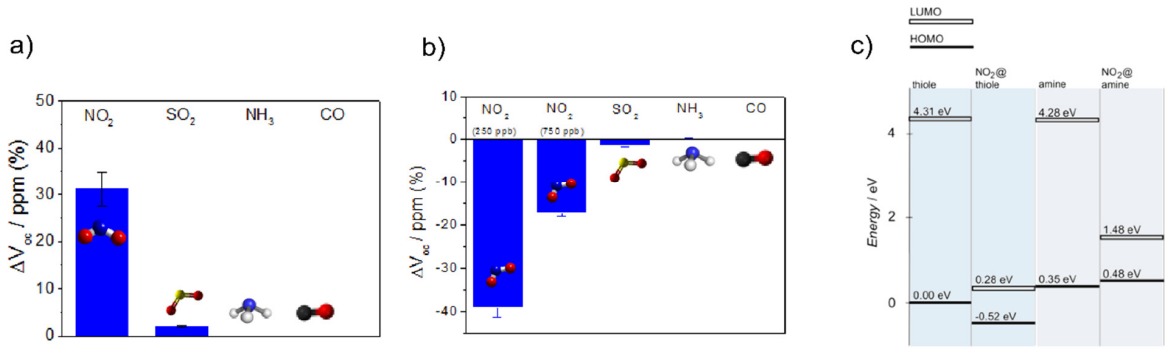

Fig. 3. Gas sensitivity values toward NO_2 in comparison to interfering species (SO_2, NH_3, and CO) for of (a) Sensor 1 (amine-functionalized); and (b) Sensor 2 (thiol-functionalized). (C) Energy levels of the HOMO and LUMO of the SAM functionalities without adsorbed NO_2 and with adsorbed NO_2 where the HOMO level of the isolated thiol SAM is set to 0 for convenience.

The thiol modified ZnO NWs (Sensor 2) showed a negative and nonlinear response toward different NO_2 concentrations (see figure 2 b, c) in comparison to the Sensor 1. The observed inverted sensor signals for Sensor 1 and Sensor 2 with different SAMs functionalities demonstrate the critical role of gas–surface interactions of the sensor.

Figure 3 a, b shows the selective response of Sensor 1 and Sensor 2 towards NO_2 in comparison to other common interfering and combustion gases such as SO_2, NH_3 and CO which were tested at significantly higher concentrations (2.5–25 ppm). As can be seen, both functionalized sensors show significantly lower responses toward the tested interfering gases which indicate a successful selective detection at room temperature. Through investigating the SAM–NO_2 binding geometries and positions of the energy levels of the SAM and the most-stable SAM–NO_2 systems, The DFT calculations indicate that the lowest unoccupied molecular orbital (LUMO) level of the SAM–gas system for both cases (amine and thiol) is much lower than in the NO_2-free case (see figure 3c). Additionally, the relatively low position of the LUMO of thiol–NO_2 and relatively high position of the highest occupied molecular orbital (HOMO) of amine–NO_2 implies a predominantly electron-acceptor character for first system and a predominantly electron-donor character for the second system which can explain the experimentally observed reversed signals the two functionalized sensors.

4. Conclusion and outlook

A self-powered gas sensors based on hybrid inorganic-organic system were developed to selectively detect low NO_2 concentrations without any external power sources. The open circuit voltage, the self-generated sensor signal, was induced by p-Si/n-ZnO diodes upon visible light illumination. The surface modification of n-ZnO surface with amine and thiol terminated organic SAMs enabled a selective sensing as well as facile gas-surface interaction at room temperature without the need activation energies neither thermal heating nor UV illumination. Moreover, the DFT simulations of binding interactions of the SAM-NO_2 and consequent changes of the organic surface HOMOs is the key factor that determines the gas response of such hybrid material toward different gases. These hybrid organic/inorganic systems provide new paradigms for the development of highly selective gas sensors, where organic modifications tailor the surface properties of MOx in a controllable fashion to interact with specified gases.

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